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Preparation of Monodisperse Polystyrene Latices by γ-Ray Polymerization and Their Electron-Microscopic and Electrophoretic Characterization

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The preparation of monodisperse polystyrene latices by the initiation with γ-rays from ^{60}Co is described. The latices were prepared by the direct polymerization method in the presence of the emulsifier Aerosol MA. The latex samples were characterized with regard to the particle size, the particle size distribution, and the surface particle charge by the methods of electron microscopy and moving boundary electrophoresis. The surface properties of latex particles were examined on samples exhaustively dialysed against distilled water and treated with ion-exchange resins. The results were compared with data collected on latices prepared by persulfate initiation. The latices prepared by γ-ray initiated polymerization proved to have a somewhat smaller particle size and a higher degree of monodispersity in a wider range of the emulsifier concentration than those prepared by persulfate initiated polymerization. Whereas with persulfate initiation monodisperse latices were obtained at emulsifier concentrations near to the critical micelle concentration, with irradiation initiation monodisperse samples were formed at higher emulsifier concentrations. It was found that the mechanism of polymerization in the presence of Aerosol MA deviates from those formulated by Smith and Ewart. From data on electrophoretic mobility of particles the zeta-potentials and particle surface charge densities for various prepared latices were calculated. On the basis of measurements of electrophoretic mobility in relation to pH values of latex suspensions the character of functional groups which contributed to the total particle surface charge is discussed.

INTRODUCTION

In the last years we have published several papers on monodisperse polystyrene latices. Some of them refer to the synthesis of monodisperse latices[1] and light scattering on latex particles[2,3]. Others report on the protein binding on the surface of latex particles[4] and the stability of latices in immunochemical systems[5,6], also on their use in medical serology[7,8]. As all these studies were performed by using latices synthesized by chemical initiation and whose surface is chemically heterogeneous owing to the presence of different functional groups, we needed a method for the preparation of monodisperse polystyrene latices with chemically homogeneous particle surfaces.

From this point of view the method of the initiation of γ-ray polymerization has been selected in order to obtain samples as monodisperse as possible. Experiments of this kind have appeared all the more interesting in view of the fact that the literature on emulsion polymerization by irradiation initiation is very scarce. Unlike chemical initiation, the high-energy γ-irradiation offers a source of free-radical initiation which varies only negligibly with temperature and time. γ-rays produce free radicals in both the aqueous phase and in the particles, and this was used for checking some kinetic parameters in emulsion polymerization by Vanderhoff et al.[9]. Their study, however, did not aim at obtaining monodisperse latices. Stannet et al.[10] reported on the preparation of a latex sample whose particle size distribution range was narrower than the one obtained by chemical initiation and the total dose needed for a complete conversion was below 0.05 Mrad.

Latex samples prepared in our study by γ-irradiation were characterized by the methods of electron microscopy and electrophoresis. The purpose of the study was to determine conditions for the preparation of monodisperse latices by γ-irradiation initiated polymerization and to compare their properties with those of the latices obtained by chemical initiation.

<div align="center">EXPERIMENTAL</div>

Materials

Styrene monomer of 99.9% purity was obtained by the courtesy of the Organska kemijska industrija, Zagreb, Yugoslavia. It contained about 15 p.p.m. t-butyl-catechol as inhibitor and was stored at —20 °C. Immediately before polymerization the inhibitor was removed by a threefold extraction with 10% sodium hydroxide solution.

The emulsifier Aerosol MA (sodium dihexylsulfosuccinate, obtained by the courtesy of American Cyanamid Co., Wayne, N. J., U.S.A.) was used without further purification.

Nitrogen used in chemically initiated polymerization was taken without purification, while the nitrogen used in γ-rays initiated polymerization was purified by conducting it through a heated column with BTS catalyst (BASF, Ludwigshafen, Germany) for the elimination of oxygen traces.

All other chemicals were of reagent grade purity.

Preparation of Latices

The reaction mixture for the synthesis of latices by γ-rays irradiation was prepared according to the recipe given in Table I. The mixtures were put into large glass test tubes (27 cm long and 3 cm in diameter) provided with openings for the inlet and outlet of nitrogen. Each test tube was equipped with a micromotor with a glass stirrer. The test tubes were inserted into the central part of a [60]Co γ-rays source of the external type constructed at the Institute »Ruđer Bošković«. After mixing in a nitrogen atmosphere for 20 min the reaction mixtures were exposed to irradiation at room temperature. During the polymerization process each reaction mixture was continuously mixed in a nitrogen atmosphere. The γ-ray dose rate was 95 000 rad/h and the reaction time varied in relation to the total dose required.

<div align="center">TABLE I</div>

General Recipe for Preparation of Monodisperse Polystyrene Latices by the γ-Ray Initiated Polymerization with Aerosol MA as Emulsifier

Monomer: styrene	20%*
Emulsifier: Aerosol MA	0.625—1.250%
Water	up to 100%

* All percentages are by weight.

In order to compare the irradiation prepared latices with those obtained by chemical initiated polymerization, previously prepared latices[1] were partially used. They had been prepared by the direct polymerization method (at 50 °C) and the seeding polymerization method with potassium persulfate as the initiator in both procedures. Also a series of latices were specially prepared by the direct polymerization method as described earlier[1] but at the reaction temperature of 70 °C.

Determination of Residual Styrene

The residual styrene content of the prepared latices was determined by extracting a latex sample with a certain volume of iso-octane and determining the styrene content of the iso-octane extract spectrophotometrically at the wavelengths 282 and 291 nm, by a modification of the method proposed by Newell[11] and McGovern et al.[12]. 1 ml of the latex suspension was extracted with 5 ml iso-octane by shaking for 24 hours. In all cases this procedure appeared sufficient for complete extraction as shown in preliminary experiments. To avoid a jelly-like structure frequently appearing after shaking, the suspension was centrifuged at about 2500 g for 15 minutes. 1 ml of iso-octane layer was diluted with a certain volume v (ml) of pure iso-octane in order to obtain the concentration range suitable for measurements. The styrene concentration, c (g/ml), in the prepared latex was expressed as

$$c = 5 (1 + v) (D_{282}/k_{282}) \tag{1}$$

where D_{282} is the optical density at 282 nm and k_{282} the slope of the calibration straight line. In the concentration range of 6.9×10^{-5} to 27.6×10^{-5} g/ml the value of k_{282} calculated by the least squares method was 3.31×10^{-3}.

Measurements of optical density were made on a Beckman Model DU spectrophotometer, using cells of 10 mm light path length.

Particle Size Determination

The particle size of the latices was determined by electron microscopy. A Trüb, Täuber & Co., electron microscope (Model KM-4) was used and the measurements of the particle size were made directly from electron micrographic plates as described elsewhere[1]. About 300 particles for each sample were measured for the particle size distribution evaluation. The precision of these measurements was ±4 nm.

Electrophoretic Measurements

In order to remove the emulsifier left from polymerization as well as other oxidation and decomposition products, all latex samples were extensively dialyzed against distilled water for 8 days. For that purpose the Visking seamless cellulose tubing (Union Carbide Corp., Chicago, Ill., U.S.A.) was used. The dialysis procedure was the same as described by Ottewill and Shaw[13] and was performed with latex suspensions diluted to 2% concentration. The concentration of the dialyzed latex was determined gravimetrically after evaporation of about 10 ml of suspension to dryness in a water bath and drying the solid remainder in vacuum at room temperature over night.

The latex suspension for moving boundary electrophoretic experiments contained about $10^{11} - 10^{12}$ particles per milliliter. For that purpose a series of dilutions was made volumetrically from a stock latex suspension by adding solutions of sodium chloride and, in order to obtain the required pH value, sodium hydroxide or hydrochloric acid, so that the total ionic strength, μ, was constant (5.0×10^{-2} mol/l). Buffered latex suspensions were dialyzed for 24 hours against pure buffer solution of the same ionic strength to avoid a disturbance of the boundary due to osmotic flow. Immediately before measurements a sucrose solution was added to the latex suspension, in order to facilitate the rapid formation of a sharp boundary. The final concentration of the added sucrose solution amounted always to 0.5% and was found to have practically no effect on electrophoretic mobility[14]. The pH value of each system under investigation was controlled immediately before measurement by an electronic pH-meter in conjunction with an Ingold glass electrode.

The electrophoretic mobility for some systems was determined also after deionizing latex samples with a mixture of cation and anion exchange resins. The ion-exchange resins used were 20/50 mesh Dowex 50W-X4 and Dowex 1-X4 (Fluka AG., Buchs SG, Switzerland). The resins and latices were treated by the procedure proposed by Vanderhoff et al.[15]. The deionized latex suspensions were dialyzed in the above described way, except in the case of two suspensions of latex LS 225 at pH 4.25 and 5.10. These were not dialyzed for 24 hours because of a spontaneous coagulation, and the electrophoretic mobility was therefore measured immediately after the addition of electrolyte solutions and sucrose.

The electrophoretic mobility was determined by the Tiselius moving boundary method, using two techniques of measurements. The main part of the experiments was performed by using a relatively simple moving boundary apparatus constructed according to the design of Ottewill and Shaw[14] (Technique A). The electrophoresis cell was put into a thermostat bath (Townson & Mercer Ltd., Croydon, England) at (25.00 ± 0.05) °C. After temperature equilibration the initial boundary was adjusted into a convenient position for observation by slow addition of the latex suspension by means of a peristaltic pump (Perpex, LKB, Sweden). A stabilized rectifier (Electrophoresis Power Supply, MA 8902, Iskra, Kranj, Yugoslavia) was used as a source of constant power and direct current. The applied voltage was about 100 V and the respective current 5—7 mA. The migration of the boundary was followed several times during electrophoresis by a cathetometer (W. G. Pye & Co., Ltd., Cambridge, England) allowing readings to be made with a precision of ± 0.005 cm. The potential gradient E in V/cm was calculated as the ratio between the difference of potential on the measuring electrodes and the distance between these electrodes measured by the cathetometer. The difference of potential was measured by a calibrated voltmeter with a precision of $\pm 2^0/_0$. The duration of a typical experiment was about 30 minutes.

For the other part of the experiments a Portable Electrophoresis Apparatus, Ser. F-780 (American Instrument Co., Silver Spring, Md., U.S.A.) was used (Technique B). Latex suspensions having a concentration from 8.1 to 32.4×10^{-4} g/ml were employed. The pH and the specific conductance were checked before and immediately after the mobility measurement for each sample. The Tiselius electrophoresis cell of cross-section 1.52 cm $\times$ 0.21 cm was thermostated at (25.0 ± 0.1) °C by circulating water from a constant-temperature bath. The moving boundary was determined by the interference optical method. The position of the boundary in certain time intervals was seen as a sharp transition from interference fringes into a uniformly lighted strip. For taking photographs sheet film of 20 DIN sensitivity was used at a magnification of 2.11 : 1. The light wavelength was 546 nm and the time of each exposure was 24 seconds. The electrophoretic velocity was determined by measuring the migration of interference fringes as a function of time directly from photographs by a measuring projector (»Nipon«, Japan) allowing the measurement of length to be made with a precision of 0.002 mm. The potential gradient E was determined by measuring current I flowing through the cell and determining the specific conductance a of the suspension separately and applying Ohm's law $E = I/aA$, where A is the cross-sectional area of the cell at the point of observation. All the measurements were made with a current of 2.5 mA.

RESULTS

The preliminary attempts to prepare monodisperse latices by γ-ray initiated polymerization have shown that for a relatively satisfactory conversion of styrene a dose as large as 1.5 Mrad is necessary. This is obvious from Fig. 1 which shows the dependence of the residual monomer on the total dose of irradiation. The best results were obtained by varying c_E, the emulsifier concentration from 0.625 to $1.250^0/_0$ at a constant monomer concentration of $20^0/_0$. The particle size generally decreased as the emulsifier concentration increased as shown in Table II which gives the particle size distribution parameters for different samples of polystyrene latices and its dependence on the emulsifier concentration used. Also data on the residual styrene content in the prepared latices are presented. Each sample is characterized by arith-
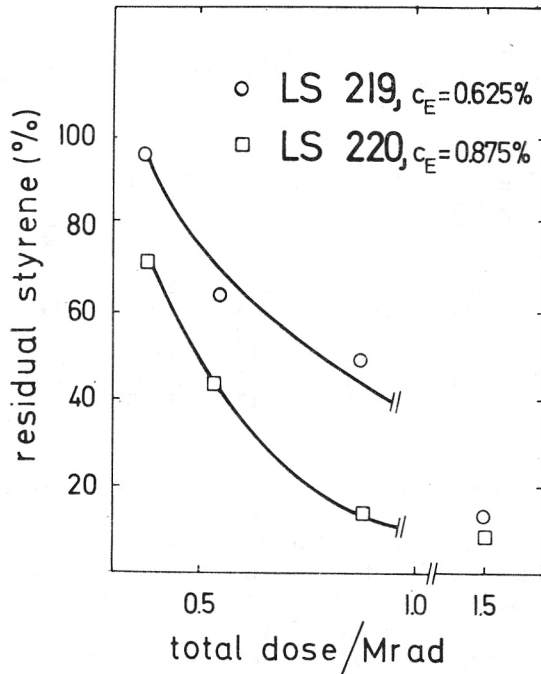
Fig. 1. Dependence of the residual styrene on the total dose of irradiation.

TABLE II

Particle Size Distribution Parameters of Polystyrene Latices Prepared by γ-Ray Initiation with Aerosol MA as Emulsifier at Room Temperature. γ-Ray Dose Rate: 95 000 rad/h; Total Dose: 1.5 Mrad

Sample	Emulsifier %	Residual Monomer Styrene %	$\bar{D}$/nm	D_n/nm	D_w/nm	$s(D)$/nm	$s(\bar{D})$/nm	P
LS 219-4	0.625	>10	190.9	191.8	194.5	13.2	0.66	1.040
LS 215	0.875	9.8	151.6	151.9	152.9	4.4	0.38	1.008
LS 220-4	0.875	9.0	122.0	122.4	123.8	8.2	0.42	1.035
LS 225	1.000	4.1	119.1	119.3	119.5	3.2	0.15	1.006
LS 216	1.125	4.2	132.5	132.5	132.9	3.5	0.31	1.006
LS 226	1.125	3.8	74.3	74.7	75.4	5.4	0.45	1.033

metic mean diameter $\bar{D}$, number average diameter D_n, weight average diameter D_w, standard deviation of the distribution $s(D)$, standard error $s(\bar{D})$ and polydispersity ratio $P = D_w^3/D_n^3$. All these quantities are defined and computed as described earlier[16]. As seen from the values of P, the degree of monodispersity of prepared latices is satisfactorily high.

TABLE III

Particle Size Distribution Parameters of Polystyrene Latices Prepared by Persulfate Initiation. Polymerization Time: 11.5 hours at 70 °C

Sample	Emulsifier %	Residual Monomer Styrene %	$\overline{D}$/nm	D_n/nm	D_w/nm	$s(D)$/nm	$s(\overline{D})$/nm	P
LS 205	0.50	1.45	232.6	233.5	235.7	15.4	0.85	1.028
LS 206	0.75	1.25	170.8	172.8	176.0	18.9	1.05	1.057
LS 54-PJ	0.75	—	137.6	139.2	141.8	14.2	0.64	1.066
LS 207	1.00	0.93	115.5	123.8	138.7	33.2	1.81	1.405
LS 208	1.25	1.10	77.4	82.5	94.1	20.7	1.05	1.493
LS 209	1.50	0.66	100.1	103.7	111.3	20.2	0.96	1.235

Table III gives particle size data on polystyrene latices prepared by the direct polymerization method using potassium persulfate as the initiator at 70 °C. The reaction time was 11.5 hours. Comparing data in Table II and Table III it may be seen that the latices prepared by γ-ray initiated polymerization have a somewhat smaller particle size and a higher degree of monodispersity in a wider range of emulsifier concentration than those prepared by chemically initiated polymerization. In all cases of latices prepared by chemical initiation the conversions were very near 100%; this is in good agreement with our earlier findings[1]. On the basis of our earlier experience we are inclined to think that the decrease in the average particle size obtained in the case of latex LS 54-PJ, as compared with latex LS 206, was due to the aged solution of emulsifier used. Fig. 2 shows the dependence
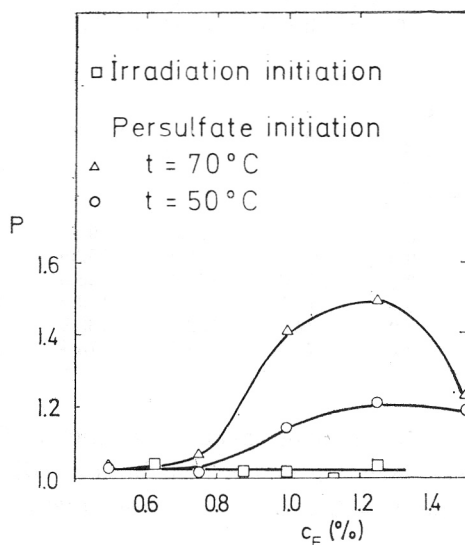

Fig. 2. Dependence of the polydispersity ratio P on the concentration of the emulsifier Aerosol MA for polystyrene latices prepared by the γ-ray and persulfate initiated polymerizations.

of the polydispersity ratio P on the concentration of the emulsifier Aerosol MA for polystyrene latices obtained by γ-ray initiation at room temperature and initiation with potassium persulfate at 50 and 70 °C. Data concerning the procedure at 50 °C are taken from our previous paper[1].

In order to interpret our results in terms of the theory of emulsion polymerization by Smith and Ewart[17], the logarithmic plots D_n $vs.$ c_E (concentration of emulsifier) were drawn. The obtained straight lines shown in Fig. 3 prove
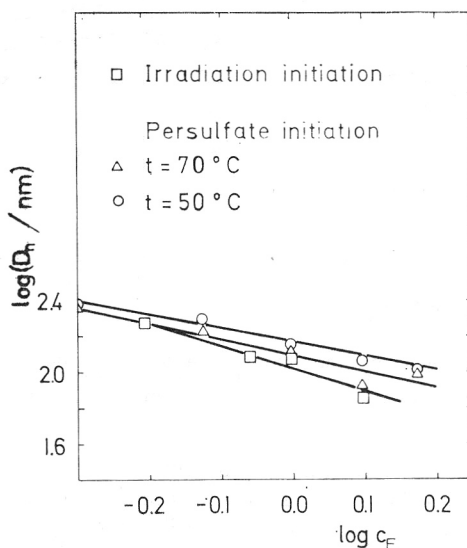

Fig. 3. Dependence of log (D_n/nm) on log c_E for polystyrene latices prepared by the γ-ray and persulfate initiated polymerizations.

that D_n is a power function of c_E. The slopes of the lines calculated by the least squares method amounted to -1.11 ± 0.38 for latices obtained by γ-ray initiation and -0.89 ± 0.20 for latices obtained by persulfate initiation at 70 °C.

Electrophoretic mobility as a function of concentration was determined at a constant ionic strength of 5.0×10^{-2} mol/l and at the constant pH value of 11.4 for each sample of polystyrene latices. At this pH value all ionic groups on the surface of latex particle are completely dissociated[14] and electrophoretic mobility is therefore the measure of the electrokinetic particle surface charge. It has been found that the particles of all samples were charged negatively. In all cases the migration of the boundary was a linear function with respect to time over the period of the run. The electrophoretic velocity was calculated by the least squares method. The average standard deviation on the obtained values was no more than $\pm 2\%$. Figs. 4 and 5 show the relationship between the mobility u and concentration for latices prepared by chemical and γ-ray initiation, respectively. Darkened points denote the mobility values obtained by extrapolation to zero concentration. These values were employed to calculate zeta-potentials ζ and the particle surface charge densities σ. The mobilities were converted into zeta-potentials using the computations of Wiersema et $al.$[18]. The particle surface charge density σ was calculated using the equation[19]

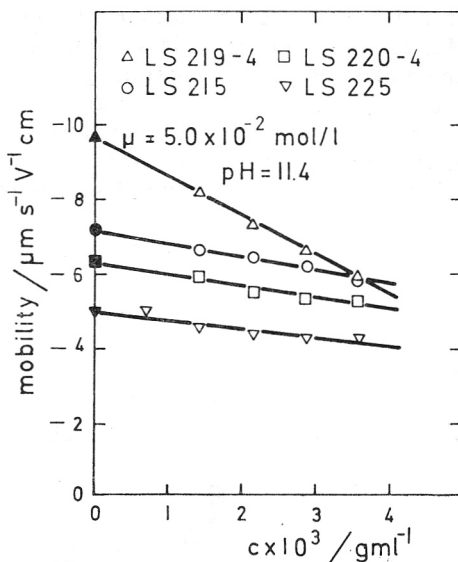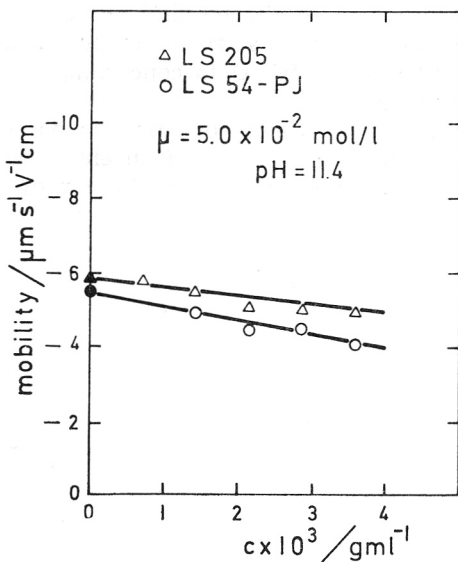$$\sigma = (4n\varepsilon/\varkappa)\ \sinh\ (Z/2) \qquad (2)$$

Fig. 4. Dependence of electrophoretic mobility on the concentration of latices prepared by the persulfate initiated polymerization.
Fig. 5. Dependence of electrophoretic mobility on the concentration of latices prepared by the γ-ray initiated polymerization.

where n is the ionic concentration in ions/cm³, ε the electronic charge and $\varkappa$ the Debye-Hückel parameter ($1/\varkappa$ is the so-called »thickness« of the diffuse double layer). Parameter Z is defined as $z\varepsilon\varkappa/kT$, where z is the valence of the counter ion, k the Boltzmann constant and T the absolute temperature.

The equation (2) was derived for the flat double layer, but the error in applying it to spherical particles is rather small for large $\varkappa r$ values, where r is the particle radius[20]. For a 1-1 electrolyte and an aqueous medium at 25 °C the expression (2) combined with Smoluchowski equation[21] reduces to

$$\sigma = 35\,200\ c_m^{1/2}\ \sinh\ 0.25u \qquad (3)$$

where c_m is the molar concentration of electrolyte and u the electrophoretic mobility expressed in μm s⁻¹ V⁻¹ cm. The particle surface charge density is expressed in e.s.u. cm⁻² (1 e.s.u. = 3.33564×10^{-10} C).

Data on electrophoretic mobilities u, zeta-potentials ζ, and surface charge densities σ, for particles of differently prepared polystyrene latices are given in Table IV. By dividing the values σ with the elementary charge of one ion the number of ions per unit of particle surface was obtained (last column in Table IV). As may be seen from the values obtained for zeta-potentials and surface charge densities all the investigated latices belong to the group of latices with a high charge density on the particle surface. This may explain their exceptional stability, even when they are totally dialyzed against distilled water.

For the characterization of functional groups on the particle surface the electrophoretic mobility of latex particles was analysed in relation to the pH suspension values at a constant concentration of suspension and a constant ionic strength. For that purpose three different polystyrene latices were

TABLE IV

Electrophoretic Mobilities u, Zeta-Potentials ζ, and Surface Charge Densities σ for Various Prepared Monodisperse Polystyrene Latices at 25 °C. pH = 11.4; Ionic Strength, μ = 5.00 × 10⁻² mol/1

Sample	D/nm	u/μm s⁻¹ V⁻¹ cm	ζ/mV	$\sigma \times 10^6$/C cm	$N_{el} \times 10^{-13}$ cm
Persulfate Initiation — Direct Polymerization Method					
LS 54-2*	197.3	—5.76ᵇ	—81.7	6.16	3.85
LS 205	233.5	—5.86ᵃ	—78.4	5.35	3.35
LS 54-PJ	137.6	—5.42ᵃ	—74.5	4.72	2.95
Persulfate Initiation — Seeding Polymerization Method*					
LS 97-10	398.8	—6.64ᵇ	—90.2	7.31	4.57
LS 137-5	531.2	—6.14ᵇ	—82.5	6.23	3.89
LS 142-4	729.2	—4.94ᵇ	—64.2	4.28	2.68
LS 145-4	942.4	—3.76ᵇ	—48.8	2.88	1.80
Irradiation Initiation					
LS 219-4	190.9	—9.50ᵃ	—149.5	14.10	8.82
LS 215	151.6	—7.02ᵃ	—98.9	7.40	4.62
LS 220-4	122.0	—6.14ᵃ	—87.4	5.83	3.65
LS 225	119.1	—4.96ᵃ	—69.4	4.16	2.60

ᵃ Determined by Technique A; ᵇ Determined by Technique B;
* For data on the preparation and particle size characterization of latices see Ref. 1.

analysed. Latices LS 205 and LS 142-4, were prepared by the direct polymerization method and the seeding polymerization method, respectively, with potassium persulfate as initiator, while the latex LS 225 was obtained by the γ-rays initiated polymerization. The behaviour of the above mentioned latices after deionization with a mixture of ion-exchange resins was also investigated. The results obtained are shown in Figs. 6, 7, and 8. Owing to the coagulation of the system, it was difficult to determine the mobility of the deionized LS 225 sample in the pH range below 5.5, while for values below 4 this proved altogether impossible.

It should be noted that after the treatment of LS 225 with the mixture of ion-exchange resins, different interference colours were observed on the latex surface and along the flask wall. By shaking the flask the colours would disappear and appear again after a short time, their intensity increasing as time passed. This was due, according to Vanderhoff et al.[15], to the light diffraction on the so-called »liquid crystals«, i. e. on the latex particle aggregates packed in orderly arrays. The explanation of this phenomenon, according to these authors, lies in that the ion exchange not only desorbs the emulsifier from the particle surface but also removes the electrolyte from the aqueous phase. This decrease in electrolyte concentration increases the thickness of the double layer, so that the neighboring particles interact with one another at greater distances. Thus the difference in the distance between the particle centers becomes great enough to give different interference colours. We noticed these colours only in the samples of a certain minimum concentration (about 1⁰/o), and this is also in agreement with the findings of Vanderhoff et. al.[15].
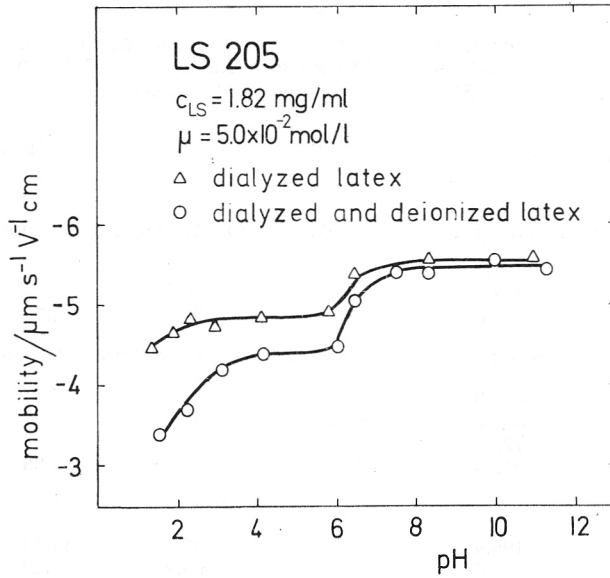
Fig. 6. Electrophoretic mobility against pH values for polystyrene latex LS 205 prepared by the persulfate initiation using the direct polymerization method.
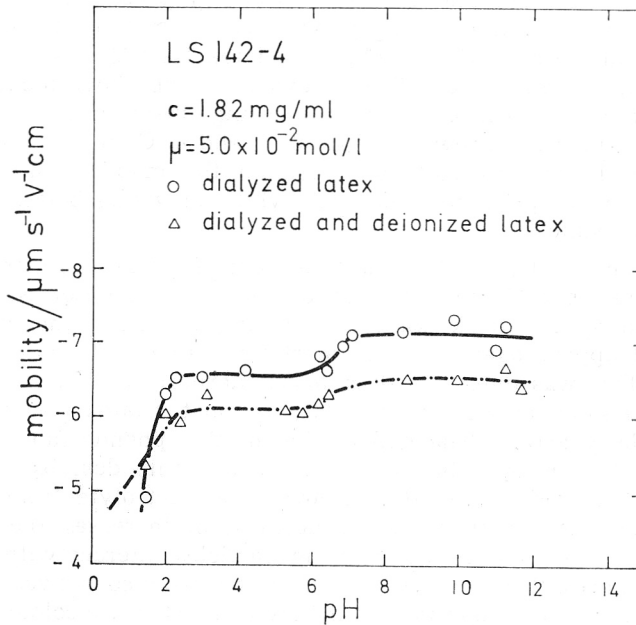

Fig. 7. Electrophoretic mobility against pH values for polystyrene latex 142—4 prepared by the persulfate initiation using the seeding polymerization method.
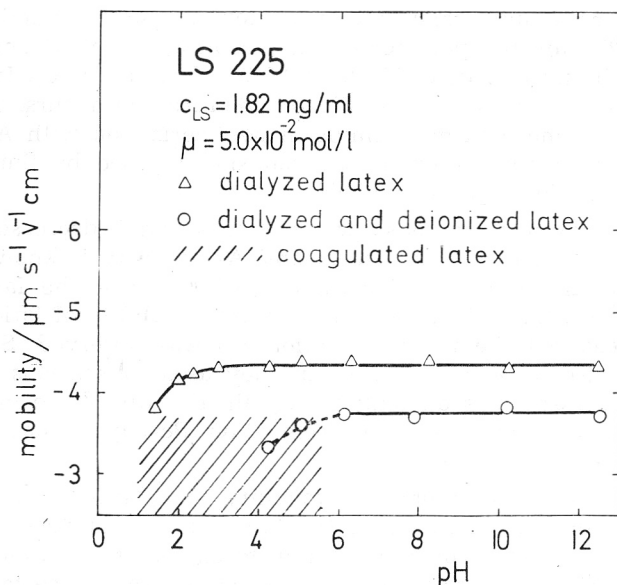
Fig. 8. Electrophoretic mobility against pH values for polystyrene latex LS 225 prepared by the γ-ray initiated polymerization.

DISCUSSION

Our experiments suggest that it is possible to prepare monodisperse polystyrene latices by γ-ray irradiation in a wider range of emulsifier concentration than in the case of the initiation with potassium persulfate. In addition, while with persulfate initiation the monodisperse latices are obtained at an emulsifier concentration near the critical micelle concentration[1], in irradiation initiation it seems that the monodisperse latices are formed also at higher emulsifier concenrations. The conversion of monomer styrene into polystyrene increases with increased emulsifier concentration. Our experiments have not confirmed the findings of Stannet et al.[10], according to which the dose of 0.05 Mrad was sufficient for a good conversion. As may be seen from Fig. 1 (latices LS 219 and LS 220), to achieve a fairly good conversion of monomer styrene it is necessary to increase the total dose to as much as 1.5 Mrad and even with this dose the conversion is less complete than in chemical initiation. As we do not know the experimental details in the work of Stannet et al.[10], we cannot say how these differences came about.

According to Smith and Ewart's theory of emulsion polymerization[17], the number of particles per unit volume, N, should be a function of the emulsifier concentration, $N \sim c_E^a$. Since $N \sim D_n^{-3}$, consequently $D_n \sim c_E^{-(a/3)}$. Provided that the emulsifier is present in a micellar form the value of the exponent should be $a = 3/5$. From the slopes of the lines log D_n vs. log c_E (Fig. 3) we calculated the values of the exponent a in the case of γ-ray initiated polymerization ($a = 3.33 \pm 1.14$) and the persulfate initiated polymerization ($a = 2.67 \pm 0.60$). Statistical testing showed no significant difference between these two values which both differ significantly from 3/5. Significantly higher values of a when using Aerosol MA as the emulsifier in polymerizations

initiated with potassium persulfate were found also by Vanderhoff *et al.*[9] ($a = 2.538 \pm 2.253$ for the polymerization performed at 50 °C and $a = 2.306 \pm 0.385$ at 70 °C) and Deželić *et al.*[1] ($a = 2.605 \pm 0.155$ at 50 °C). It may be seen that all the above values are statistically identical with ours. This confirms the claim that the mechanism of emulsion polymerization with Aerosol MA as the emulsifier does not follow the mechanism proposed by Smith-Ewart, no matter what initiation type is involved.

Electrophoretic mobility, as shown in Figs. 4 and 5, decreased with increased concentration of the latex suspensions. As viscosity is known to increase with concentration[22], this may explain the behaviour of the latex. It should be noted, however, that when the electrophoretic mobility of latices by technique B was measured the reverse relationship was observed. Similar results were obtained also by Force *et al.*[23], but they used suspensions containing an emulsifier. At present it is difficult to explain this difference in the obtained relationship between mobility and concentration. Perhaps it may have resulted from different equipment used.

Measurements of electrophoretic mobility in relation to pH values may cast some light on the character of the latex particle surface. In our latices the particle surface was covered with different kinds of functional groups which contributed to the total particle surface charge. A certain number of these charges surely originated from adsorbed molecules of the emulsifier. In the literature the opinions diverge as to the possibilities of eliminating of the adsorbed emulsifier. Some authors[15,23-25] claim that it is impossible to remove the emulsifier completely from the particle surface by dialysis only, while others[13,14] consider it to be possible. We tried therefore to clarify this question by analysing latices LS 205 and LS 225 after dialysis and after their treatment with ion-exchange resins. The form of the curves, *i. e.* the presence of the inflexion points (Figs. 6 and 7) indicates the presence of several kinds of functional groups on the latex surface as has been evidenced also in other polystyrene latices[14]. The inflexion point for LS 205 (Fig. 6) at about pH = 6 is likely to characterize the carboxyl group. A high degree of mobility in the dialyzed sample in the low pH range from 1.5 to 2.0 comes from the groups with pK values higher than those of the carboxyl group. It may therefore be assumed that this is due to the presence of sulfate groups covalently bound to the particle surface and also to the presence of sulfonate groups adsorbed on particles. After deionization the carboxyl groups remained, while the mobility at low pH values was reduced. This is explained by the removal of the adsorbed emulsifier (the sulfonate groups), while the remaining mobility originated from sulfate groups. The carboxyl groups, like the sulfate ones, are bound covalently to the particle surface; they appear in the course of polymerization. The sulfate groups come from the sulfate radicals produced by the decomposition of persulfate molecules, whereas carboxyl groups are due to the oxidation of the chain end by persulfate or the present oxygen.

The curve for latex LS 142-4 (Fig. 7) prepared by the seeding polymerization method using potassium persulfate shows the same pattern as the curve for LS 205 prepared by the direct method. This shows that regardless of the preparation method, at chemical initiation, the surface characteristics of the latices obtained are the same, but they differ from the characteristics of latex LS 225 obtained by irradiation initiated polymerization.

The curve of LS 225 (Fig. 8) before deionization shows a relatively high latex particle electrophoretic mobility which diminishes after deionization. In the dialyzed latex there is only one inflexion point which may be ascribed to the presence of sulfonate groups belonging to the emulsifier adsorbed on the latex particle surface. The inflexion point on the curve of the deionized latex, at pH=4.25, may be apparent because the latex suspension at pH $<$ 5.5 was not dialyzed against the electrolyte before electrophoretic measurements because of coagulation which appeared spontaneously as early as an hour after the sample preparation. Owing to the missing dialysis before the electrophoresis experiments it was not possible to establish the Donnan equilibrium, and for this reason the lower mobility may have been due to a somewhat higher ionic strength of the system of 5×10^{-2} mol/l. As systems at pH values below 5.5 coagulate spontaneously, the actual shape of the electrophoretic curve as a function of pH cannot be ascertained. The only explanation for the appearance of spontaneous coagulation is in that the process of deionization reduces the particle surface charge density to a value below the critical one required for the stabilization of latex particles.

The results shown in Figs. 6 and 8 point to the conclusion that the deionization procedure, carried out as in our experiments and being the same as the procedure of Vanderhoff et al.[15], cannot completely remove sulfonate groups. This raises the question of whether this is due to inefficient procedure or to a strong (perhaps covalent) binding of the molecular species carrying sulfonate groups on the latex particle surface — the binding occurring under conditions under which latices were synthesized in our experiments. As the radiolysis of aqueous systems produces radicals but cannot produce carboxyl groups and the possibly formed hydroxyl groups cannot be electrophoretically identified, we are inclined to think that the presence of carboxyl groups on latices obtained by irradiation initiation is not probable.

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SAŽETAK

Priređivanje monodisperznih polistirenskih lateksa polimerizacijom pomoću γ-ozračivanja te njihova elektronsko-mikroskopska i elektroforetska karakterizacija

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Opisano je priređivanje monodisperznih polistirenskih lateksa dobivenih inicijacijom s pomoću γ-zraka iz ^{60}Co. Lateksi su priređeni metodom direktne polimerizacije u prisutnosti emulgatora Aerosola MA. Dobiveni lateksi karakterizirani su s obzirom na veličinu i raspodjelu veličina čestica te njihov površinski naboj metodama elektronske mikroskopije i elektroforeze s pomičnom granicom. Ispitivanje površinskih svojstava čestica lateksa vršeno je s uzorcima iscrpno dijaliziranim prema destiliranoj vodi kao i obrađenim pomoću ionskih izmjenjivača. U svrhu usporedbe vršeni su i eksperimenti s lateksima dobivenim s pomoću persulfatne inicijacije. Nađeno je da se inicijacijom γ-ozračivanjem dobivaju lateksi visoke monodisperznosti u širem rasponu koncentracije emulgatora nego kod persulfatne inicijacije. Dok se kod persulfatne inicijacije monodisperzni lateksi dobivaju kod koncentracija emulgatora bliskih kritičnoj koncentraciji miceliranja, kod inicijacije ozračivanjem monodisperzni uzorci nastaju kod viših koncentracija emulgatora. Nađeno je da je mehanizam reakcije polimerizacije u prisutnosti Aerosola MA drugačiji od mehanizma formuliranog u Smith-Ewartovoj teoriji emulzijske polimerizacije. Iz podataka o elektroforetskoj gibljivosti čestica izračunani su zeta-potencijali i površinska gustoća naboja čestica, a na osnovi zavisnosti između elektroforetske gibljivosti čestica i pH suspenzije lateksa razmatran je karakter funkcionalnih skupina koje određuju površinski naboj čestica.

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